

Design and Control of a Process to Extract β -Carotene with Supercritical Carbon Dioxide

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A strategy for locating optimal designs is applied to the extraction of β -carotene with supercritical CO_2 . With the modified Peng-Robinson equation of state to estimate the phase equilibria, models are developed to simulate the three-phase (solid, liquid, and supercritical fluid) extraction and separation processes. The design optimization minimizes the annualized cost while producing β -carotene of the desired quality. The results demonstrate that despite high operating pressures, supercritical extraction can be competitive for the recovery of high-value products at low production rates. Furthermore, the increases in solubility with small amounts of cosolvent can have a substantial impact on the economics of the proposed design. An example is given in which the addition of 1% ethanol to the CO_2 solvent transforms an unfavorable design into a competitive one. In addition, a dynamic model is proposed for the product separator, and its differential-algebraic equations are integrated with DASSL. Proportional (P) and proportional-integral (PI) control schemes are studied to maintain the pressure by manipulating the vapor flow rate. Although the set-point response of the PI controller is acceptable, disturbance rejection is poor. A disturbance in the feed flow rate causes lower quality β -carotene to be produced. The desired quality is maintained when the separator is oversized, but this raises the annualized cost.

Introduction

Supercritical extraction (SCE) has been investigated for a variety of separations (McHugh and Krukonis, 1986). Promising examples include the recovery of cholesterol from butterfat (Novak et al., 1988), eicosapentanoic acid from fish oils (Krukonis, 1988), and caffeine from coffee and tea (Brunner, 1988). However, only a few of the applications have been implemented on a commercial scale, and consequently, little is known about the design and operation of these processes.

Recently, Cygnarowicz and Seider (1988, 1989) formulated a strategy for designing cost-efficient SCE processes. In this approach, a model is developed for the process flow sheet, and a nonlinear program (NLP) is created to minimize either the utility or annualized cost for the product specifications. Until now, the strategy was applied to the dehydration of acetone with use of supercritical CO_2 . This system was chosen because extensive, high-pressure, phase equilibria data are available (Panagiotopoulos and Reid, 1987), and the critical properties are known. Acetone is a commodity chemical, however, and it was concluded that SCE is not competitive with conventional dehydration processes due to the high equipment costs. Furthermore, it was postulated that SCE could be competitive for the separation of high-value products, like β -carotene, at low production rates.

In this paper, the potential for extracting β -carotene with supercritical CO_2 is explored. β -Carotene is a lipid-soluble, yellow- to orange-red pigment present in the flow-

ers, fruit, and roots of plants, as well as in fungi and bacteria. Because it is the precursor to vitamin A in the human metabolism, β -carotene is used in food processing to impart a uniform color and vitamin A enrichment to a wide variety of food products. In addition, recent clinical studies indicate that β -carotene may play a significant role in the prevention of many forms of cancer (Menkes et al., 1986). These findings may help to increase the market for this chemical as a food additive, since the public perception of food products enriched with a cancer preventative should be very positive. At the present time, the bulk of the β -carotene used commercially is manufactured by chemical synthesis. However, plant materials containing large amounts of β -carotene, such as carrots and palm oil, offer the possibility of obtaining "natural" β -carotene through extraction with nontoxic, supercritical CO_2 . In addition, industrial production of β -carotene by fermentation has been reported, where the product is isolated by a process of solvent washings and crystallizations (Ninet and Renaut, 1979). Alternatively, extraction with supercritical CO_2 may allow the isolation of natural β -carotene directly from the fermentation broth. Since β -carotene sells for \$60-88/kg (depending on the quality), the high operating and capital costs of SCE can be tolerated.

Cygnarowicz et al. (1989) measured the equilibrium solubility of pure β -carotene in supercritical CO_2 at temperatures from 313 to 343 K and pressures up to 420 bar. The highest solubilities were reported at 343 K and pressures in excess of 405 bar. In addition, solubilities were measured in binary mixtures of CO_2 and 1% ethanol, 1% methanol, and 1% methylene chloride, on a weight

basis. The cosolvent increased the solubility in every case, with the largest increase in the binary mixture of CO₂ and ethanol. Pure-component properties (i.e., vapor pressure, critical temperature and pressure, and acentric factor) were estimated for β -carotene and the experimental data used to estimate the interaction coefficients for the modified Peng–Robinson equation of state (Panagiotopoulos and Reid, 1986).

In this paper, the model for β -carotene solubility in supercritical CO₂ is utilized in the design optimization of a process to extract β -carotene from fermentation broths. Models are prepared to simulate the extraction and separation steps, and the previously mentioned design strategy is used to locate optimal designs. In addition, a dynamic model is prepared for the product separator, and the resulting differential–algebraic equations (DAEs) are integrated with DASSL (Petzold, 1982). Proportional (P) and proportional–integral (PI) controllers are investigated for maintaining the pressure in the separator. The responses of the controllers to changes in the set point and to disturbances in the feed flow rate are examined.

Modeling the Steady-State SCE Process

Simulation of the β -carotene purification process necessitates making several simplifying assumptions. First, the small amounts of vegetable or animal oil that may be present in the medium are neglected, and it is assumed that the liquid portion of the fermentation broth is pure water. Second, the mass-transfer limitations of the cell walls are ignored (the product of the fermentation process is endocellular), and the β -carotene is assumed to reside in the water as a pure solid. This is not unreasonable when the fermentation broth is filtered and the cells crushed prior to extraction. Although experimentation is needed to check the simplified model, the β -carotene solubilities are at their upper limit. The result is a lower bound on the annualized cost, corresponding to the most optimistic designs.

The system to be modeled consists of three species (CO₂, β -carotene, H₂O) that partition among three phases (solid, liquid, supercritical fluid). Since β -carotene is virtually insoluble in water, and since the liquid contains very little CO₂, it is assumed that no β -carotene dissolves in the liquid phase and that the solid phase is pure β -carotene. Furthermore, steady-state, continuous operation is assumed. Therefore, for a given temperature and pressure, the equations to be solved in the extractor and separator are

$$f_1 - v_1 - S = 0 \quad (1)$$

$$f_i - v_i - l_i = 0 \quad i = 2, 3 \quad (2)$$

$$\frac{v_1}{V} \Phi_1^V P - P_1^{\text{sat}} \exp\left(\frac{V_s(P - P_1^{\text{sat}})}{RT}\right) = 0 \quad (3)$$

$$\frac{v_i}{V} \Phi_i^V - \frac{l_i}{L} \Phi_i^L = 0 \quad i = 2, 3 \quad (4)$$

$$\sum_{i=1}^3 v_i - V = 0 \quad (5)$$

$$\sum_{i=2}^3 l_i - L = 0 \quad (6)$$

where the subscript 1 refers to β -carotene and 2 and 3 refer to CO₂ and H₂O, respectively; f_i are the flow rates of species i in the feed to the equilibrium stage; Φ_i^V is the fugacity coefficient of species i in the vapor phase; Φ_i^L is

the fugacity coefficient of species i in the liquid phase; P_1^{sat} is the vapor pressure of solid β -carotene, V_s is the molar volume of solid β -carotene, T is the temperature, P is the pressure, and R is the gas constant. The fugacity coefficients are computed by the modified Peng–Robinson equation of state (PR-EOS; Panagiotopoulos and Reid, 1986). The unknowns are the flow rates of species i in the liquid, l_i , the flow rates of species i in the vapor, v_i , the flow rate of β -carotene in the solid phase, S , and the total liquid and vapor flow rates, L and V , respectively. The Newton–Raphson method is used to solve the equations. Initial guesses for the flow rates of CO₂ and H₂O are generated by calculating the vapor–liquid equilibria of the feed, with β -carotene excluded, using the SEPSIM flow sheet program (Andersen and Fredenslund, 1987). An initial guess for the β -carotene in the supercritical stream is obtained from eq 1, assuming the stream contains only CO₂ and β -carotene. These guesses are excellent, and convergence of the equations is normally achieved in 3–4 iterations.

The model for the separator assumes the continuous removal of solid β -carotene and water. This is considered to be a reasonable idealization as the flow rates of the β -carotene and water phases represent a small fraction of the separator throughput. Furthermore, the density of the β -carotene–water mixture is approximated as that of water at the temperature and pressure of the separator. The dense β -carotene–water mixture is assumed to settle to the bottom of the separator where it can be collected with a series of valves that can be periodically opened to release the solids that accumulate. The details of the design calculations are summarized in the Appendix.

The subroutines for the extractor and separator were incorporated into a model for the process flow sheet, which includes the heat exchanger, cooler, and compressors shown in Figure 1. Since the interaction coefficients for the modified PR-EOS are known over a small range of temperature (313–343 K), this model could not be used to estimate the heating, cooling, and compression loads. Instead, the group contribution equation of state (GC-EOS) of Skjold-Jorgensen (1984, 1988) was used, and the small amounts of β -carotene in the process streams were neglected.

A NLP was created to minimize the annualized cost of the process. It was solved with an infeasible path strategy (Biegler and Cuthrell, 1985) and the successive quadratic programming method (Powell, 1977). The proposed design produces 8930 kg of β -carotene/year, or approximately 25% of the world market.

Minimum Annualized Cost

In this formulation, the extractor temperature (T_e) and pressure (P_e), the separator pressure (P_s), the flow rate of solvent makeup ($F_{\text{CO}_2}^{\text{makeup}}$), and the tear stream temperature and flow rates (which include the flow rate of the solvent recycled to the extractor, $F_{\text{CO}_2}^{\text{rec}}$) are adjusted to minimize the annualized cost. The annualized cost is the sum of the annual cost of utilities and the cost of the installed equipment, multiplied by the annual rate of return on investment (assumed to be 15%). The utility costs arise from compressing the solvent and make-up streams, preheating the feed stream, and cooling the solvent recycle stream. The utility cost coefficients are given in the Appendix. The installed cost of the equipment was determined through correlations of the graphical data in Ulrich (1984). These correlations, along with the overall heat-transfer coefficients, are also given in the Appendix.

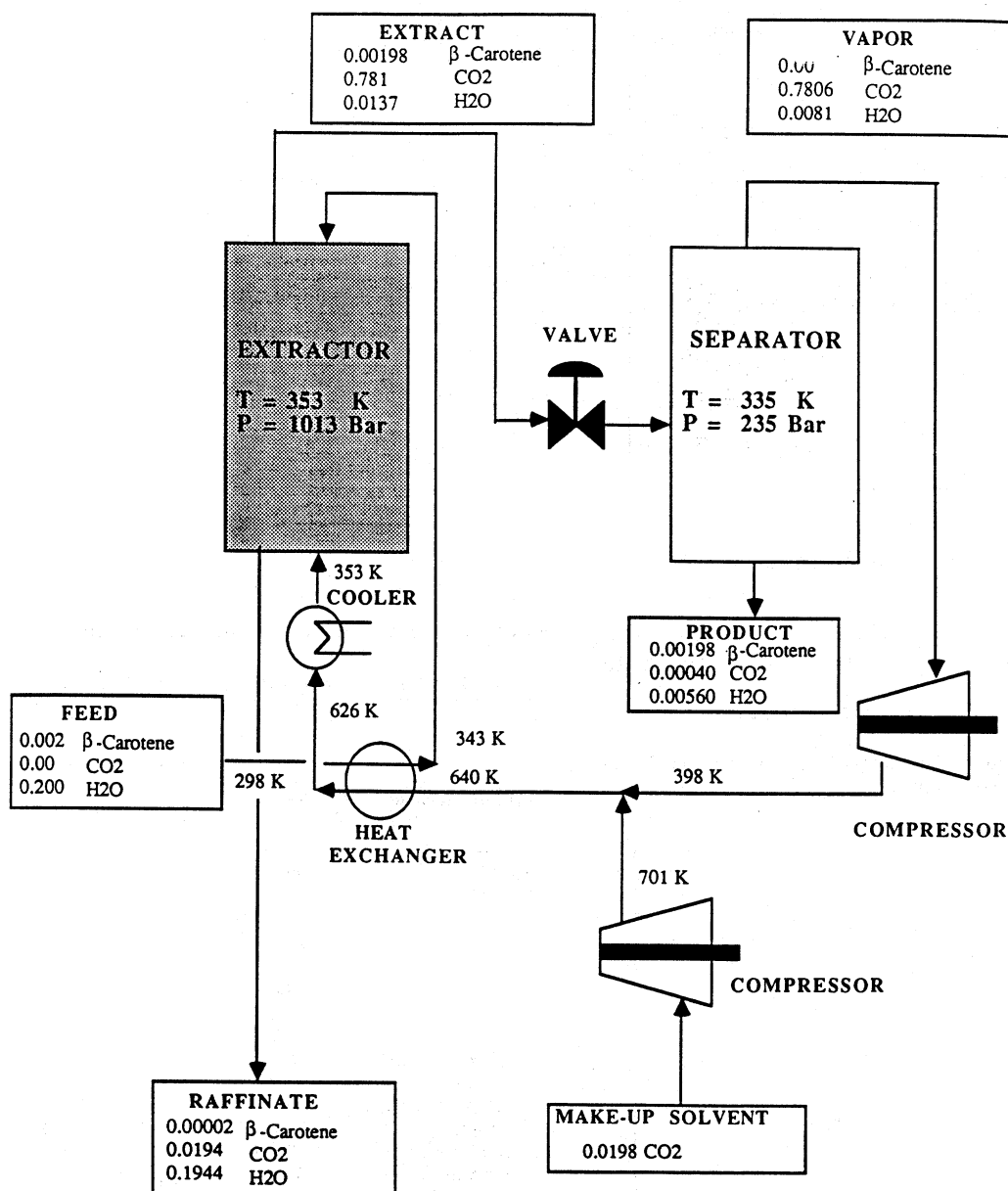


Figure 1. Process to extract β -carotene from water using supercritical carbon dioxide.

Included in the NLP, in addition to the tear equations, are a recovery constraint that stipulates that the product contains at least 99% of the β -carotene in the feed stream, a quality constraint that requires that the solid plus liquid products be at least 90% β -carotene by weight and a nonnegativity constraint on the flow rate of the solid in the raffinate stream.

Consideration must also be given to the residence time of the β -carotene in the extractor, since it may decompose at high temperatures. In several experiments, Bruno (1989) used a reaction screening apparatus (Bruno and Hume, 1985) to investigate the decomposition of the β -carotene-water slurry at 353 K. The slurry was held in a glass-lined, stainless steel pressure vessel for 30 and 120 min, typical of its residence time in the extractor. Then, the experiment was rerun with powdered stainless steel added to the slurry. Significant degradation of the β -carotene was observed, especially with the addition of the powdered stainless steel. It is noted that Bruno and Straty (1986) discuss the impact of such powdered materials on decomposition reactions, in general. Another experiment was run using powdered quartz (fused silica), and this showed little degradation of the β -carotene

in 120 min. In all of the experiments, samples of the slurry, with and without the powdered materials, were analyzed by high-pressure liquid chromatography. On the basis of the encouraging results with powdered quartz, the residence times were bounded at 2 h for extractions at 353 K and 4 h for extractions at 343 K in the design optimizations discussed below.

Case 1: $T_e \leq 343$ K. The highest temperature at which equilibrium solubility data are available is 343 K, which was specified as the upper bound for T_e in case 1. The results of the design optimization are at the upper bounds for T_e (343 K) and P_e (1013 bar) and are given in Table I. Even at these extreme conditions, the low solubility of β -carotene requires that 11.487 kmol/h of CO₂ be recirculated to recover 99% of the product. The product quality constraint was relaxed (from 90 to 70 wt %) since the extremely high solvent recirculation rate precluded obtaining a product containing only 10 wt % water. The utility costs for the design are reasonable (\$2805/year) because, at such high pressures, the fluid is very dense and recompression costs are small. However, the equipment costs are high due to the high solvent recirculation rate. Eight extractors (0.66-m diameter) and three separators (0.99-m

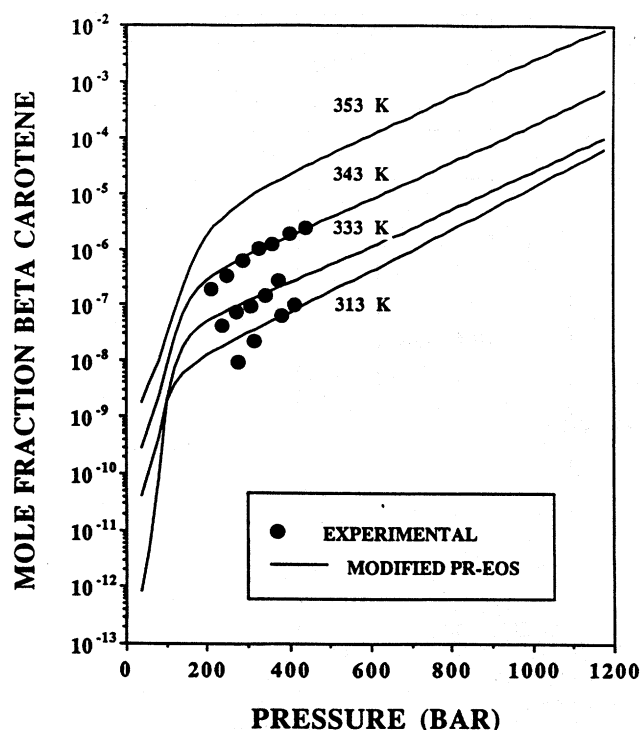


Figure 2. Mole fractions of β -carotene in supercritical CO_2 as a function of pressure and temperature.

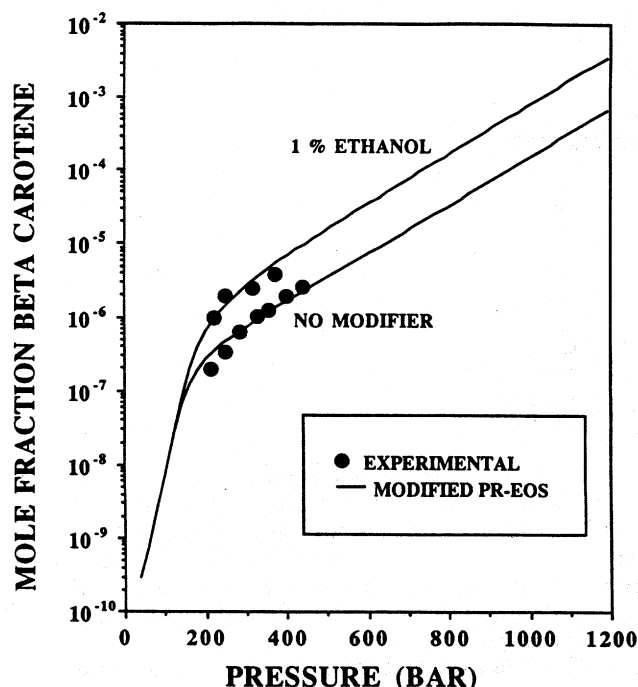


Figure 3. Mole fractions of β -carotene in supercritical CO_2 doped with 1% ethanol as a function of pressure at 70 °C.

diameter) are arranged in parallel to process the large volumes of solvent, giving an annualized cost of \$1 231 000/year or \$137.85/kg β -carotene. Clearly, this design is not competitive.

Case 2: $T_e \leq 353$ K. Since the solubility of β -carotene increases with temperature (Cygnarowicz et al., 1989), the upper bound on T_e was relaxed from 343 to 353 K. Although no experimental data are available at 353 K, estimates are obtained from the modified PR-EOS with the interaction coefficients at 313, 333, and 343 K correlated as a function of temperature. Estimates of the mole

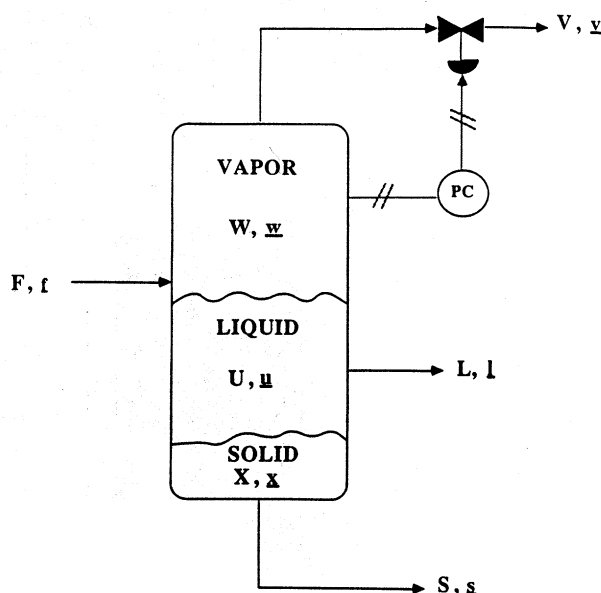


Figure 4. Schematic of the three-phase separator.

Table I. Design for Minimum Annualized Cost

	case 1	case 2	case 3 CO_2 /1% ethanol	case 4 over- design
product recovery, %	99	99	99	99
product quality, wt %	70	90	90	92.5
P_e , bar	1013	1013	1013	1013
T_e , K	343	353	343	353
P_s , bar	459	234.9	473	287.5
$F_{\text{CO}_2}^{\text{make}}$, kmol/h	0.019 91	0.019 76	0.027 02	0.019 80
$F_{\text{CO}_2}^{\text{rec}}$, kmol/h	11.487	0.781	2.280	0.779
product, kmol/h				
β -carotene	0.001 980	0.001 980	0.001 980	0.001 980
CO_2	0.001 769	0.000 408	0.000 570	0.000 31
H_2O	0.020 99	0.005 566	0.005 146	0.004 04
total cost of utilities, \$/year	2805	358	602	354
equipment costs, \$				
compressors	320 600	119 000	186 200	121 600
heat exchangers	39 120	6650	14 070	6560
extractors	5 463 000	385 700	1 240 000	778 100
no. of units	8	2	2	2
diameter, m	0.66	0.35	0.59	0.35
residence time, h	4	2	3.8	2
separators	2 006 000	158 900	620 000	285 300
no. of units	3	1	1	1
diameter, m	0.99	0.45	0.76	0.45
annualized cost, \$/year	1 231 000	174 000	309 100	179 100
cost/kg of β -carotene, \$/kg	137.85	19.48	34.61	20.05

fractions at 353 K, as well as the experimental and theoretical values at the other temperatures, are shown in Figure 2. Note that the estimates at 353 K are significantly higher than those at the lower temperatures, and the theoretical estimates at all temperatures are qualitatively similar.

The results of the optimization are also presented in Table I. Note that P_e and T_e are at their upper bounds (1013 bar and 353 K), but the recirculation of CO_2 is much lower, 0.781 kmol/h. The product recovery and quality constraints are active at 99% and 90 wt %, respectively. Since $F_{\text{CO}_2}^{\text{rec}}$ has been substantially reduced, the utility and equipment costs are much lower. For this design, two extractors, having diameters of 0.35 m, and one separator, having a diameter of 0.45 m, are required. The annualized cost is \$174 000/year or \$19.48/kg of

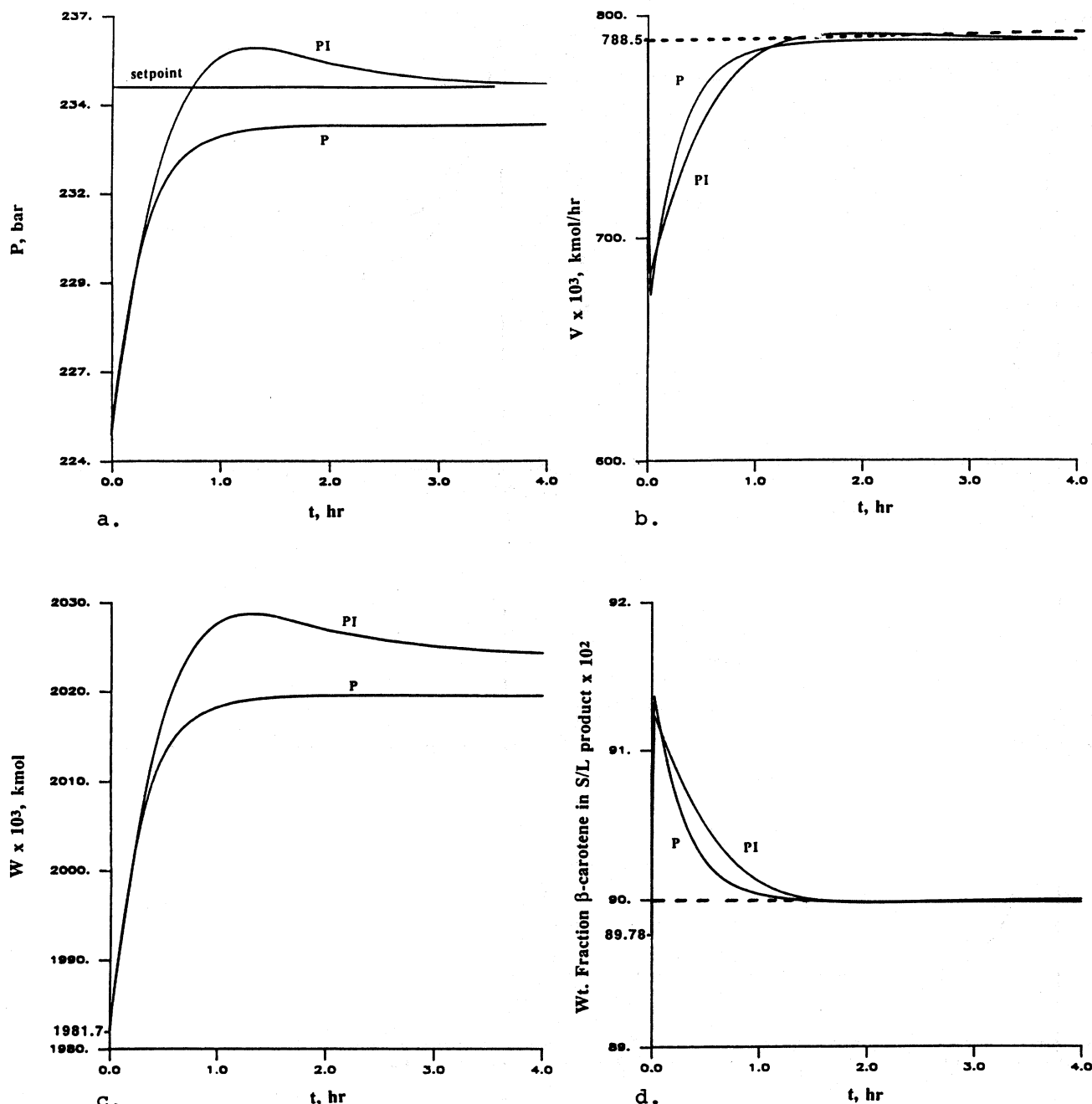


Figure 5. Closed-loop responses to step change in separator pressure.

β -carotene. It is noted that, for many fermentation processes, the cost of separation is less than or equal to 40% of the selling price of the product (i.e., \$24–32 for β -carotene). On this basis, such a design appears to be competitive.

Case 3: $T_e = 343$ K, CO_2 with 1% Ethanol. Finally, extraction with 99% CO_2 and 1% ethanol was considered. The experimental studies (Cygnowicz et al., 1989) indicated that the cosolvent increased the solubility of β -carotene 2–5 times over its solubility in CO_2 . Because experimental data were not available for the solubility of β -carotene in ethanol, the CO_2 /ethanol mixture was modeled as a pseudocomponent, and the modified PR-EOS was used to estimate the solubility of β -carotene in the pseudocomponent. Mixture critical properties were computed for the pseudocomponent, and interaction coefficients were estimated from the experimental data for the solubility of β -carotene in the CO_2 /ethanol mixture. A comparison of the experimental and theoretical mole

fractions of β -carotene in CO_2 and in the pseudocomponent at 343 K are shown in Figure 3.

The results of the design optimization using the doped solvent are given in Table I. In this case, T_e is fixed since experimental data for β -carotene in CO_2 /1% ethanol are not available as a function of the temperature. At the optimum, P_e is at its upper bound (1013 bar), $F_{\text{CO}_2}^{\text{rec}}$ is 2.280 kmol/h, and the product recovery and quality constraints are active. Note that a significant reduction in the solvent recirculation rate is obtained, as compared to case 1, resulting in an annualized cost of \$309 100/year or \$34.61/kg of β -carotene. Note that the cost is nearly 75% less than the annualized cost obtained at 343 K with no cosolvent.

The validity of the pseudocomponent assumption was investigated by performing a vapor–liquid equilibrium calculation (using the GC-EOS) for the ethanol–water– CO_2 stream entering the separator, assuming the small amount of β -carotene to be negligible. Since 99.75% of

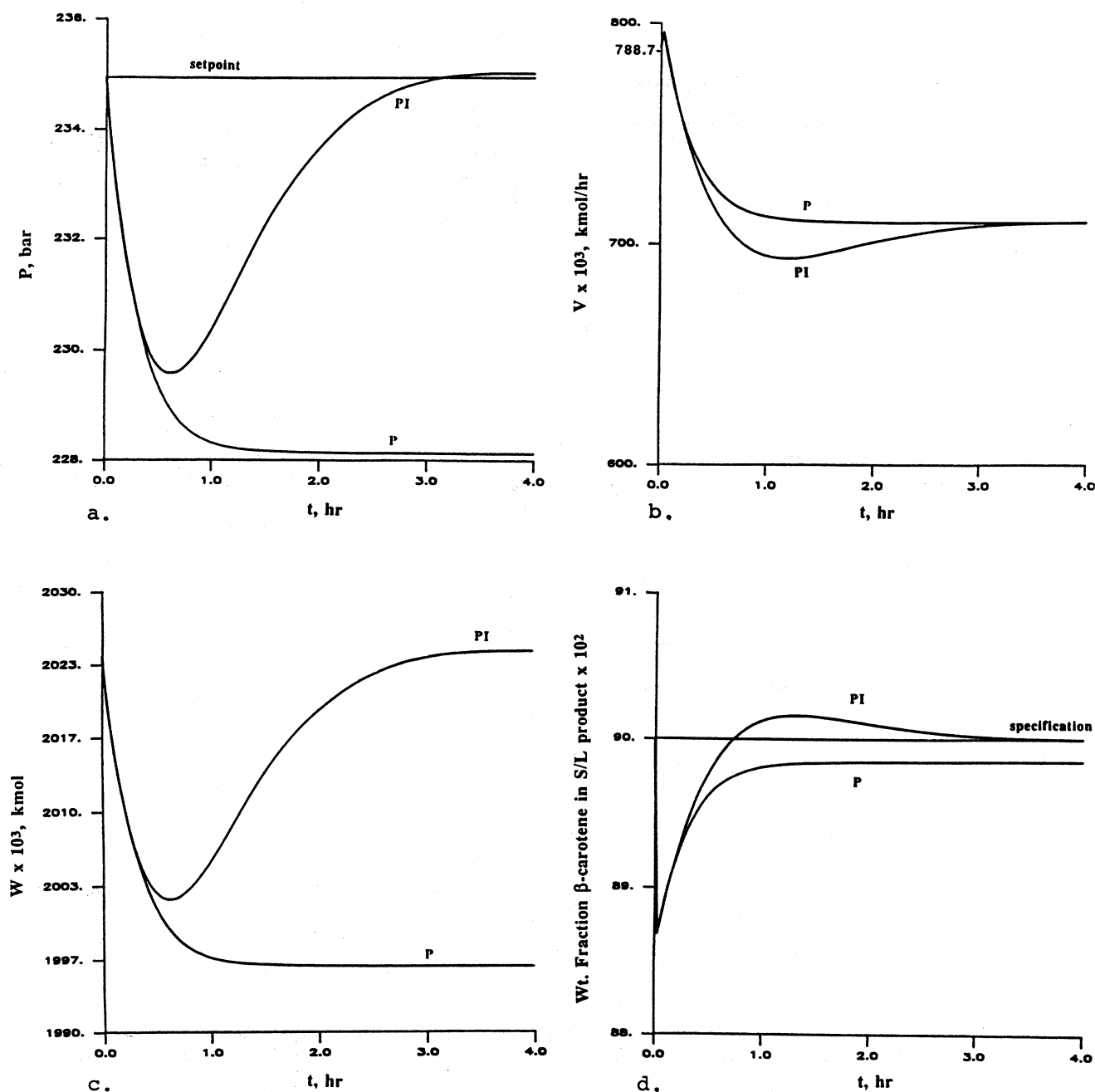


figure 6. Closed-loop responses to 10% decrease in the feed flow rate, case 2.

the ethanol was computed to remain in the CO_2 phase, the pseudocomponent assumption is valid.

The design optimizations demonstrate that despite the high operating pressures, SCE can be competitive for the recovery of high-value products at small production rates. Furthermore, the solubility increases due to small amounts of cosolvent have a substantial impact on the economics of the proposed design. In this example, the addition of 1 wt % ethanol to CO_2 transformed an unprofitable design into a profitable one.

Thus far, most design studies for SCE have focused on the steady state. These studies are complicated by operation in the critical region where small changes in T and P can shift the extractor or separator from two to three or just one phase. However, the design optimization does not account for the difficulties in maintaining steady operation in the face of disturbances or uncertainties. Thus, a dynamic model for the product separator is considered next, and the performance of proportional

(P) and proportional-integral (PI) controllers to maintain the desired pressure in the separator is discussed.

Dynamic Model

At each design optimum presented above, the separator pressure is reduced as far as possible without violating the product quality constraint. Note that, at lower pressures, the solubility of water in the CO_2 phase is reduced and the water phase increases accordingly. Therefore, the dynamic analysis focuses on the separator and addresses the question of whether or not conventional control can maintain acceptable product quality. As an example, the optimal design in case 2 is investigated. Although a single case study cannot yield generalized results, it introduces some of the difficulties in controlling SCE processes and suggests methods for overcoming them.

The steady-state, three-phase equilibrium model (eqs 1-6) is extended to create a set of differential-algebraic

equations (DAEs), and the DAE solver DASSL (Petzold, 1982) is used to integrate the dynamic model. DAEs are difficult to solve because they require consistent initial conditions, the linear system solved at each step can be ill-conditioned, and the error estimates are sensitive to discontinuities, inconsistencies, and sharp changes in the dependent variables. In addition, the performance of DASSL depends upon the index of the DAEs, i.e., the number of times the equations must be differentiated to yield a set of ordinary differential equations (ODEs). DASSL solves DAEs with indexes of zero or one, and care must be taken to avoid formulating DAEs with a higher index.

In the control loop, the vapor flow rate is manipulated to maintain the set-point pressure. The volumes of the vapor, liquid, and solid holdups are fixed, and hence the moles, as well as the densities, of the holdups vary. The total volume of the vessel is determined in the design optimization, and it is assumed that the supercritical, liquid, and solid phases occupy 99%, 0.4%, and 0.6% of this volume. The volumes of the solid and liquid phases are small to shorten the residence time of the β -carotene in the separator and reduce the possibility for degradation. The three-phase separator is shown schematically in Figure 4, and its dynamic model is

$$\frac{dw_1}{dt} + \frac{dx_1}{dt} = f_1 - v_1 - s_1 \quad (7)$$

$$\frac{dw_i}{dt} + \frac{dx_i}{dt} + \frac{du_i}{dt} = f_i - v_i - s_i - l_i \quad i = 2, 3 \quad (8)$$

$$\frac{v_1}{V} \Phi_1^V P - P_1^{\text{sat}} \exp\left(\frac{V_s(P - P_1^{\text{sat}})}{RT}\right) = 0 \quad (9)$$

$$\frac{v_i}{V} \Phi_i^V - \frac{l_i}{L} \Phi_i^L = 0 \quad i = 2, 3 \quad (10)$$

$$\sum_{i=1}^3 v_i - V = 0 \quad (11)$$

$$\frac{w_i}{W} - \frac{v_i}{V} = 0 \quad i = 1, 2, 3 \quad (12)$$

$$W - \rho_v V_{\text{vapor}} = 0 \quad (13)$$

$$\sum_{i=2}^3 l_i - L = 0 \quad (14)$$

$$\frac{u_i}{U} - \frac{l_i}{L} = 0 \quad i = 2, 3 \quad (15)$$

$$U - \rho_l V_{\text{liquid}} = 0 \quad (16)$$

$$\sum_{i=1}^3 s_i - S = 0 \quad (17)$$

$$\frac{x_i}{X} - \frac{s_i}{S} = 0 \quad i = 1, 2, 3 \quad (18)$$

$$X - \rho_s V_{\text{solid}} = 0 \quad (19)$$

$$\rho_v - \frac{P}{z_v RT} = 0 \quad (20)$$

$$\rho_l - \frac{P}{z_l RT} = 0 \quad (21)$$

$$s_2 - s_2^{\text{spec}} = 0 \quad (22)$$

$$s_3 - s_3^{\text{spec}} = 0 \quad (23)$$

$$f_i - f_i^{\text{spec}} = 0 \quad i = 1, 2, 3 \quad (24)$$

The variables introduced in the dynamic model are the holdups of the species in the vapor, w_i , the holdups of

the species in the liquid, u_i , the holdups of the species in the solid, x_i , and the total holdups of the vapor, liquid, and solid phases (W , U , and X , respectively). To avoid DAEs with an index greater than 1, the assumption of a pure solid is relaxed. The flow rates of solid CO_2 and H_2O (s_2 and s_3) are included as variables but are set to arbitrarily small numbers in eqs 22 and 23. The densities of the liquid and supercritical phases (ρ_l , ρ_v) are included as variables, as are the feed flow rates f_i , $i = 1, 2, 3$, to allow for the introduction of disturbances. In addition, the equation for P control, is

$$c\{t\} - K_c(P - P_{\text{sp}}) - c_0 = 0 \quad (25)$$

where K_c is the controller gain, P_{sp} is the set-point pressure, and $c\{t\}$ is the controller signal, which, in this analysis, is the valve stem position. If the valve dynamics are neglected and the valve flow characteristic curve is assumed to be linear (Stephanopoulos, 1984), the stem position may be related to the vapor flow rate through

$$V\{t\} = \beta c\{t\} \left(\frac{\Delta P}{sg_v}\right)^{1/2} \quad (26)$$

where β is the valve constant (assumed to be unity), ΔP is the pressure drop across the valve, and sg_v is the specific gravity of the vapor. With eq 26, $c\{t\}$ and c_0 may be eliminated from eq 25. For PI control, Chang and Chen (1984) introduce a new variable, z

$$z = \frac{K_c}{\tau_I} \int_0^t (P - P_{\text{sp}}) dt \quad (27)$$

and the controller equation becomes

$$c\{t\} - K_c(P - P_{\text{sp}}) - z - c_0 = 0 \quad (28)$$

where

$$\frac{dz}{dt} - \frac{K_c}{\tau_I} (P - P_{\text{sp}}) = 0 \quad (29)$$

and τ_I is the integral time constant. The controller gains were tuned by the reaction curve method of Cohen and Coon (Stephanopoulos, 1984). The parameters given by this method were $K_c = 3.33$ for P control and $K_c = 2.94$, $\tau_I = 0.93$ for PI control.

Servo Problem

First, the closed-loop responses are examined as the set-point pressure experiences a step change from 225.8 to 234.9 bar (set point for case 2). The responses of the pressure, vapor flow rate, vapor holdup, and weight fraction of β -carotene in the liquid plus solid products are shown in Figure 5a–d. As expected, PI control is oscillatory and more sluggish than P control. Note that the pressure reaches its new set point in approximately 4 h for PI control and exhibits offset for P control (Figure 5a). The manipulated variable, the vapor flow rate, drops sharply initially (Figure 5b) but rises as the new operating point is reached. The weight fraction of β -carotene in the liquid plus solid product streams rises sharply initially, before falling to its new value. These results indicate that the product quality is maintained above its design specification during the set-point change. However, problems arise with conventional PI controllers due to unexpected disturbances, as discussed in the next section.

Load Problem

In this analysis, a 10% decrease in the feed flow rate is introduced, assuming a fixed feed composition. The closed-loop responses for P and PI controllers are illus-

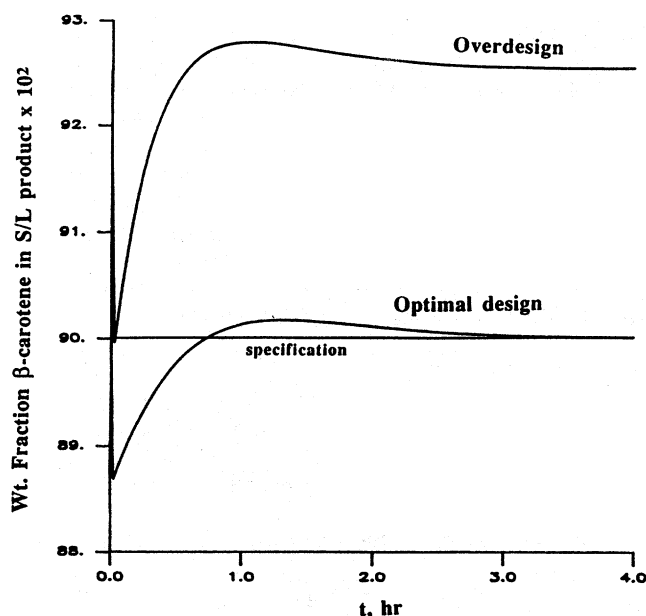


Figure 7. Closed-loop responses to 10% decrease in the feed flow rate under PI control, with and without overdiseign.

trated in Figure 6a–d. Note that with P control, the pressure drops quickly and reaches a new steady state, offset by approximately 7 bar (Figure 6a). Under PI control, a similar drop occurs, followed by a return to the set point in approximately 3 h. Although the vapor flow rate ultimately reaches the same value for P and PI control (Figure 6b), the moles of vapor in the holdup does not (Figure 6c). This variation enables the PI controller to eliminate the offset. Note also the inverse response of the vapor flow rate, which increases slightly before decreasing toward its new steady-state attractor.

The inability of the P controller to return to the set point causes the product quality to drop immediately below its specification and to remain below 90% without further intervention. The PI controller, however, eventually returns the product quality to its specification, but its response is oscillatory, and off-spec β -carotene is produced for nearly 45 min. The response time can be lowered by reducing τ_1 , however, with added oscillation and potential stability problems.

To ensure satisfactory operation for this disturbance, it is possible to overdiseign the separator. For this purpose, the design optimization was recomputed with the product quality specified at 92.5 wt % β -carotene, and the results are shown in Table I. Note that the separator pressure was increased to 287.5 bar to meet the new specification. The annualized cost for the overdiseign is \$179 100/year (\$20.05/kg of β -carotene), an increase of \$5100/year over the optimal design of case 2. The dynamic response, illustrated in Figure 7, indicates that the product quality remains above 90 wt % when the feed flow rate is decreased by 10%.

A potentially better alternative to satisfy specifications while rejecting disturbances *without* overdiseign is the implementation of advanced, model-predictive control (MPC) strategies. Such controllers are providing more effective disturbance rejection and set-point response in tightly constrained operating regions (Bregel and Seider, 1989). As models for the design of SCE processes improve, and as more experience is gained in implementing MPC schemes for complex, DAE models, it can be expected that these strategies will be applied to SCE processes, yielding more cost-effective designs.

Conclusions

Steady-state design optimizations demonstrate that SCE can be competitive for the recovery of high-value products, like β -carotene, at low production rates. The increases in solubility obtained with the addition of small amounts of cosolvent can yield a substantial decrease in the recovery cost. For the dehydration of β -carotene, the addition of 1% ethanol to the CO_2 solvent reduces the cost of the design by 75%, transforming an infeasible design into a competitive one. A dynamic analysis of the product separator indicates that although the servo response of a PI controller is acceptable, its ability to reject disturbances is poor. A 10% decrease in the feed flow rate causes the quality of β -carotene to drop below the design specifications. The product specifications are satisfied when the separator is overdiseigned (i.e., when the separator pressure is increased by 52 bar), but the overdiseign raises the annualized cost.

Notation

A	heat exchanger area, m^2
c	valve stem position, m
c_0	initial valve stem position, m
C^{comp}	installed cost of compressors, \$
C^{cw}	cost of cooling water, \$/(kJ/h)
C^{elect}	cost of electricity, \$/(kJ/h)
C^{ex}	installed cost of heat exchanger, \$
C^{ext}	installed cost of the extractor, \$
C^{sep}	installed cost of the separator, \$
D	tower diameter, m
EI	chemical engineering equipment cost index
F	feed flow rate, kmol/h
$F_{\text{CO}_2}^{\text{make}}$	flow rate of CO_2 makeup, kmol/h
$F_{\text{CO}_2}^{\text{rec}}$	flow rate of CO_2 recirculated, kmol/h
f_i	flow rate of species i in the feed, kmol/h
K_c	controller gain
K_{ab}	Souders–Brown constant, m/s
L	total liquid flow rate, kmol/h
l_i	flow rate of species i in the liquid, kmol/h
P	pressure, bar
P_e	extractor pressure, bar
P_i	suction pressure, bar
P_1^{sat}	vapor pressure of β -carotene, bar
P_s	separator pressure, bar
P_{sp}	set-point pressure, bar
R	gas constant
s_i	flow rate of species i in the solid, kmol/h
sg	specific gravity
S	flow rate of solid β -carotene, kmol/h
t	time, s
T	temperature, K
T_e	extractor temperature, K
U	total liquid molar holdup, kmol
u_i	molar holdup of species i in the liquid, kmol
u_{ag}	flooding velocity, m/s
u_t	pseudosettling velocity, m/s
V	total vapor flow rate, kmol/h; maximum molar vapor flow rate, kmol/h
v_i	flow rate of species i in the vapor, kmol/h
V_s	molar volume of pure solid, m^3/kmol
V_{liquid}	volume of separator occupied by liquid, m^3
V_{solid}	volume of separator occupied by solid, m^3
V_{vapor}	volume of separator occupied by vapor, m^3
W	total vapor molar holdup, kmol

w_i	molar holdup of species i in the vapor, kmol
W_s	shaft work, kW
X	total solid molar holdup, kmol
x_i	molar holdup of species i in the solid, kmol
z	integral windup
z_l	liquid compressibility factor
z_v	vapor compressibility factor

Greek Symbols

β	valve constant, kmol/(h·m·bar ^{0.5})
ρ	molar density, kmol/m ³
τ_I	integral time constant
Φ_i^L	fugacity coefficient of species i in the liquid
Φ_i^V	fugacity coefficient of species i in the vapor

Subscripts

l	liquid
0	initial
s	solid
sp	set point
v	vapor

Superscripts

sat	saturation
$spec$	specification

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Appendix

Utility Cost Coefficients. The following coefficients were used to compute the cost of the utilities. The values are based on 8400 operating h/year.

Cooling water cost

$$T_{in} = 300 \text{ K}, \quad T_{out} = 322 \text{ K}$$

$$\$0.07/\text{gal}$$

$$C^{cw} = \$0.00167/(\text{kJ/h})$$

Electricity cost

$$\$0.05/(\text{kW}\cdot\text{h})$$

$$C^{elec} = \$0.1167/(\text{kJ/h})$$

Equipment Cost Correlations. The equations for the cost of the equipment were correlated from the graphical data in Ulrich (1984). All equipment is constructed of stainless steel. The installed cost of the compressors as a function of the shaft work, W_s (kW), the suction pressure, P_i (bar), and the chemical engineering equipment cost index (EI) is given by

$$C^{comp} = \frac{EI}{315.0} \exp\{0.4006 \log W_s + 9.04796\} (6.9785 + 0.0186P_i)$$

Table II. Overall Heat-Transfer Coefficients

exchanger	U , (J/(m ² ·sK))
feed- raffinate exchanger	1200
solvent cooler	200

Table III. Densities (mol/L) of the Vapor and Liquid Phases in the Extractor and Separator

	case 1	case 2	case 3
extractor			
ρ_v	25.6	24.7	26.9
ρ_l	44.1	43.8	44.1
separator			
ρ_v	21.1	17.1	22.0
ρ_l	44.1	44.3	44.1

In this study, EI was 349.1. The installed cost of the heat exchangers is given as a function of the area, A (m²), and the pressure, P (bar):

$$C^{ex} = \frac{EI}{315.0} \exp[0.6489 \log \{A\} + 6.2269] (6.8069 + 0.007419P)$$

The overall heat-transfer coefficients assumed for the heat exchangers are given in Table II.

To compute the cost of the extractor, the vessel diameter is first computed. The flooding velocity (u_{sg}) is given by the Souders-Brown correlation:

$$u_{sg} = K_{sb} \left(\frac{\rho_l - \rho_v}{\rho_v} \right)^{1/2}$$

In this relationship, K_{sb} is the Souders-Brown constant, ρ_v is the vapor density, and ρ_l is the liquid density on the top tray. The densities of the vapor and liquid phases in the extractor for all cases are given in Table III. K_{sb} is assumed to be 0.064 m/s. The vessel diameter may then be calculated from

$$D = (4V/(\Pi\rho_v(0.85u_{sg})))^{1/2}$$

where V is the maximum molar vapor flow rate in the vessel. The vessel diameters are calculated with 85% of the flooding velocity. Assuming an aspect ratio of 1 for the vessel, the height is determined. The costs of vertical process vessels in Ulrich (1984) were correlated as a function of the diameter. Given the diameter, D (m), and the pressure, P (bar), the vessel cost is calculated from

$$C^{ext} = \frac{EI}{315} (5126.8D + 365.6) (2.7 + 2.1876P^{0.6218})$$

To compute the cost of the product separator, the pseudosettling velocity, u_t , is computed, assuming a liquid drop size of 100 μm :

$$u_t = 0.06 \left(\frac{\rho_l - \rho_v}{\rho_v} \right)^{1/2}$$

The densities of the vapor and liquid phases in the separator for all cases are given in Table III. With a vertical orientation, the vessel diameter may be calculated from

$$D = (4V/(\Pi\rho_v u_t))^{1/2}$$

Assuming an aspect ratio of 2, the costs of vertical process vessels in Ulrich were correlated. Given the diameter, D (m), and the pressure, P (bar), the vessel cost is calculated from

$$C^{sep} = \frac{EI}{315} (6772.4D + 323.23) (2.7 + 2.1876P^{0.6218})$$

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